"Faster G0W0 implementation for more accurate material design"

Laflamme Janssen, Jonathan ; Rousseau, Bruno ; Côté, Michel

Abstract

Traditional plane wave G0W0 calculation size is limited by two bottlenecks : the need to invert a large matrix (the dielectric matrix) and the need to carry out summations over a large number of electronic states (conduction states). The first bottleneck is caused by the choice of the basis in which the dielectric matrix is represented : traditional G0W0 implementations use a plane wave basis, which needs to be relatively large to properly describe the matrix. This talk will explain how a Lanczos basis can be generated to substantially reduce the size of the matrix. Also, the number of conduction bands needed to reach convergence in the summations is usually an order of magnitude larger than the number of valence bands. Here, the calculation of the conduction states is avoided by reformulating the summations into linear equation problems (Sternheimer equations), which also substantially reduces the computation time. Finally, we will discuss how the introduction of a model dielectric ...

Document type : *Communication à un colloque (Conference Paper)*

Faster G_0W_0 implementation
for more accurate material design

Jonathan Laflamme Janssen[1,2], Bruno Rousseau[1], and Michel Côté[1]
[1]*Université de Montréal, Canada* and *Regroupement Québécois pour les Matériaux de Pointe (RQMP)*
[2]*Université Catholique de Louvain, Louvain-la-Neuve, Belgium* and *European Theoretical Spectroscopy Facility (ETSF)*

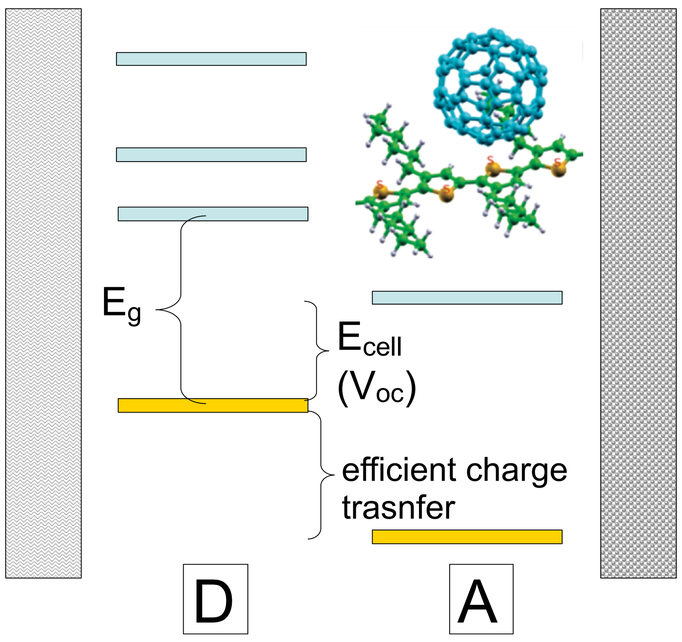
Abstract

Density-functional theory (DFT) is currently the *ab initio* method most widely used to predict electronic energy levels of new molecules. However, approximations intrinsic to the theory limit the accuracy of calculated energy levels to about ±0.5 eV. More efficient theoretical design of molecules and materials could be achieved if more precise methods were available. The G_0W_0 approach is an *ab initio* method that provides such an enhanced precision, with predicted energy levels accurate to about ±0.05 eV. However, such calculations are currently prohibitive for systems with more than a few tens of electrons, thus limiting their use in many applications. What limits calculations to this system size in traditional plane waves (PW) implementations of G_0W_0 is the need to invert the dielectric matrix in a large PW basis and the need to carry out summations over a large number of conduction states. This poster presents a strategy to avoid both of these bottlenecks.

Material design : organic photovoltaïcs

Criteria :
- Gap : optimal for solar spectrum
- Ionisation Energy (IE) :
  - lower than C_{60} (for good charge transfer)
  - high enough for good V_{oc} and air stability

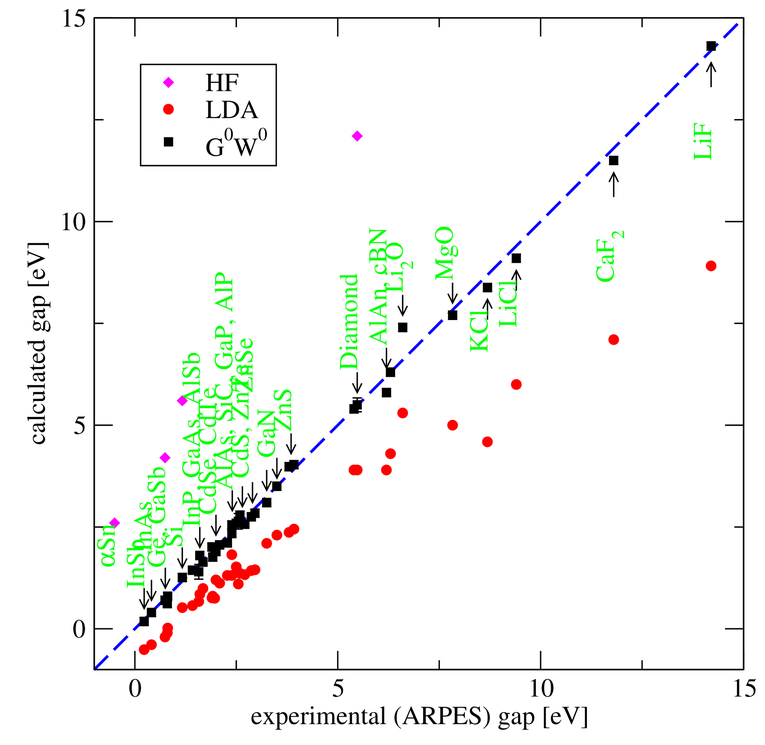
Morale: Precise electron removal and addition energies are crucial in some applications



The G_0W_0 method

DFT levels offer quick sorting of candidate materials.
Further refinement is still desirable given the ressources and time required to synthesize a new material.
G_0W_0 can provide such results

Accuracy of DFT and G_0W_0



In G_0W_0, DFT eigenstates and eigenvalues are used as a starting point :

$$\left(\hat{T}+\hat{V}_{ext}+\hat{V}_{xc}\right)|n\rangle=\varepsilon_n|n\rangle$$

They are then corrected to first order in perturbation theory using the GW exchange-correlation operator $\Sigma(\omega)$:

$$\Delta\varepsilon_n \approx \varepsilon_n+\langle n|\hat{\Sigma}(\varepsilon_n+\Delta\varepsilon_n)-\hat{V}_{xc}|n\rangle$$

The expectation value of $\Sigma(\omega)$ being :

$$\langle n|\hat{\Sigma}(\omega)|n\rangle=\frac{i}{2\pi}\sum_{n'}\int_{-\infty}^{+\infty}d\omega\,\frac{\langle n|\langle n'^{*}|\hat{\epsilon}^{-1}(\omega)\hat{v}|n'^{*}\rangle|n\rangle}{\omega-(\varepsilon_{n'}-\varepsilon_n)}$$

where $\hat{v}$ is the coulomb operator and where :

$$\hat{\epsilon}(\omega)=\hat{1}-\hat{v}\hat{P}(\omega)$$

$$\hat{P}(\omega)=\sum_{c,v}|c^{*}\rangle|v\rangle\left[\frac{1}{\omega-(\varepsilon_c-\varepsilon_v)}-\frac{1}{\omega+(\varepsilon_c-\varepsilon_v)}\right]\langle v|\langle c^{*}|$$

- O : bottleneck #1 : sum over conduction states
- O : bottleneck #2 : inversion of the dielectric matrix

Solution to bottleneck 1
Sternheimer equation

Idea : transform $\sum_c$ into a linear equation problem...

$$\hat{P}(\omega)|\psi\rangle=\sum_{c,v}|c^{*}\rangle|v\rangle\left[\frac{1}{\omega-(\varepsilon_c-\varepsilon_v)}-\frac{1}{\omega+(\varepsilon_c-\varepsilon_v)}\right]\langle v|\langle c^{*}||\psi\rangle$$
$$\equiv\sum_v|f_v^{+*}v\rangle+|f_v^{-*}v\rangle$$

$$\Rightarrow|f^{\pm}{}_v\rangle=-\sum_c\frac{|c\rangle\langle c|}{\varepsilon_c-\varepsilon_v\pm\omega}|\psi^{*}\rangle|v\rangle$$
$$=-\sum_c\frac{|c\rangle\langle c|}{\hat{H}-\varepsilon_v\pm\omega}|\psi^{*}\rangle|v\rangle$$
$$=-\frac{\hat{P}_c}{\hat{H}-\varepsilon_v\pm\omega}|\psi^{*}\rangle|v\rangle$$

Eliminating $\sum_c$

$$\Rightarrow\left(\hat{H}-\varepsilon_v\pm\omega\right)|f^{\pm}{}_v\rangle=-\hat{P}_c|\psi^{*}\rangle|v\rangle \quad \text{(Sternheimer's equation)}$$

Implementation of solution

1) H + FFTs = N logN op. ⇒ iterative method

2) H - $\varepsilon_v \pm \omega$ can be singular ⇒ SQMR instead of CG

Solution to bottleneck 2
Lanczos algorithm

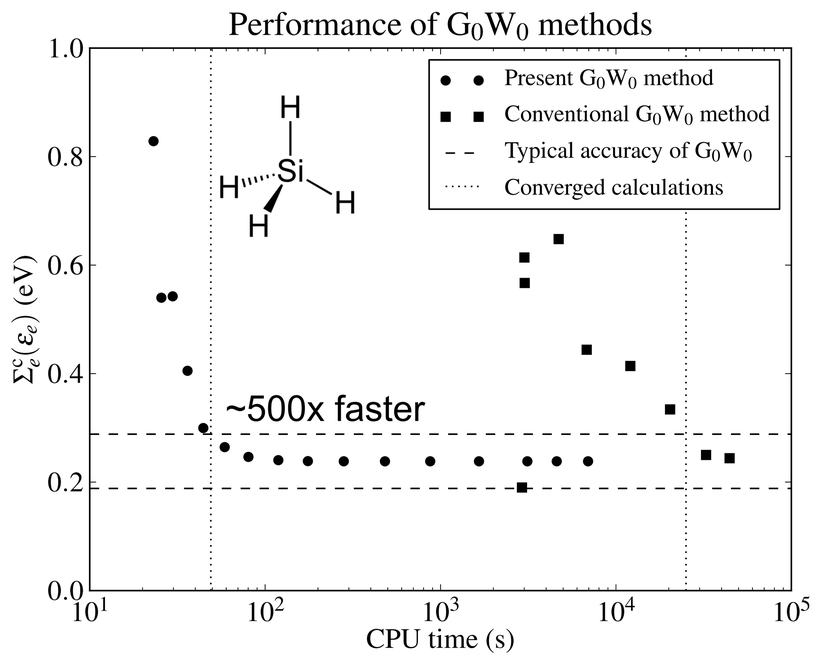
Usually, $\hat{\epsilon}(\omega)$ is expressed in a planewave basis.
Here, we decrease the size of the matrix by constructing a basis that automatically focuses on the relevant subspace :

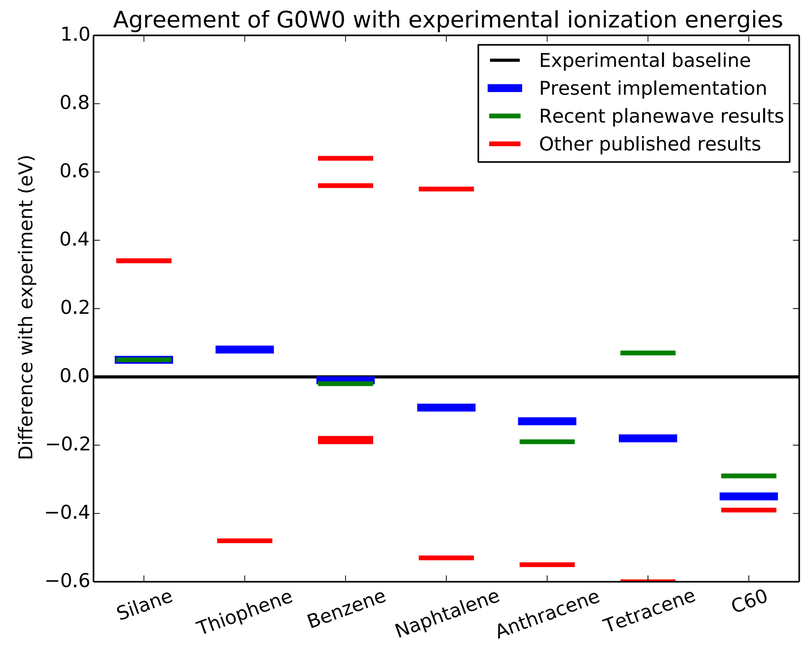
$$\left\{|\phi_0\rangle,\hat{\epsilon}(\omega)|\phi_0\rangle,\hat{\epsilon}^2(\omega)|\phi_0\rangle,\ldots,\hat{\epsilon}^N(\omega)|\phi_0\rangle\right\}$$

and then orthonormalize it to obtain the Lanczos basis :

$$\left\{|l_0(\omega)\rangle,|l_1(\omega)\rangle,|l_2(\omega)\rangle,\ldots,|l_N(\omega)\rangle\right\}$$

which is substantially smaller than a planewave basis of equivalent accuracy.





Conclusion

- 2 bottlenecks in G_0W_0 implementations :
  1. The sum over conduction states
  2. The inversion of the dielectric matrix
- We assess these bottlenecks using :
  3. Sternheimer's equation
  4. Lanczos algorithm
- and obtain a 500-fold increase in speed
- without any further approximation

See arXiv:1408.3036 for more details

Université de Montréal · RQMP · Calcul Québec · compute • calcul CANADA · Fonds de recherche Nature et technologies Québec · NSERC CRSNG · fnrs FREEDOM TO RESEARCH · ETSF · UCL Université catholique de Louvain